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Strong coherent coupling of vibronic oscillations in spheroidene

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Abstract

The four-wave mixing signals from spheroidene have been systematically investigated at various coherent periods τ. The pronounced vibronic oscillations of the fundamental modes in the ground state are clearly observed in the transient grating configuration ($\tau = 0$). Interestingly, it was found that the overtones and coupled modes become very strong compared to the fundamental modes when the signal is measured in the virtual photon-echo configuration ($\tau < 0$). The experimental results have been analyzed using a Brownian oscillator model. The intensity change with respect to the coherent period is qualitatively reproduced by the calculations. We discuss a plausible model that allows a quantitative agreement between experiment and calculation.

Keywords: Four-wave mixing; Coherent oscillations; Carotenoid; Photosynthesis; Coupled-mode

1. Introduction

The primary processes of photosynthesis involve the capture of sunlight and efficient transfer of the resulting excitation energy to the reaction centers [1, 2]. Fluorescence-excitation measurements have revealed that the efficiency of singlet-singlet energy transfer from donor carotenoid to acceptor bacteriochlorophyll molecules can be up to nearly 100% [3, 4]. It is interesting to clarify the mechanism of the highly efficient energy transfer, especially on the relationship with its dynamics. This knowledge may then make it possible to control the flow of the electronic excitations among pigments.

The dynamics of electronic states and the dissipation of the electronic excitations are strongly influenced by the dynamics of nuclei [5, 6]. Therefore, to elucidate the relationship of these dynamics, simultaneous observation of the vibronic oscillations and the electronic excitations is necessary [7]. The development of femtosecond laser sources has allowed coherent nuclear motion to be probed in real time, as well as the population dynamics of electronic

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excitations [8]. In addition to the coherent oscillations of the fundamental modes, several authors have reported the coupling between these modes [9-11] and the vibronic oscillations in the excited states [12-15]. Collective vibrational coherence among oscillating molecules can be induced when the excitation laser pulse is sufficiently short compared to the characteristic period of the mode. Recently, by properly shaping the temporal profiles of the excitation laser pulses, several authors have demonstrated the enhancement of molecular vibrational coherence as well as the population transfer between the electronic states [16-20]. For example, Hauer et al. [18] and Kanradi et al. [21] have succeeded selective excitation of the single vibrational modes of β-carotene. However, to the best of our knowledge, the artificial generation, i.e., the switching 'on' and 'off', of the coupled modes using the ultrashort laser pulses has not been attained. This is probably because of the weak intensities of such modes even in conventional Raman measurements. Nevertheless it is worthwhile to investigate the excitation of Raman inactive modes because this could open a new pathway for the use of the coherent control technique.

In the present work, the vibronic coherent oscillations of a carotenoid, spheroidene, in an organic solvent have been investigated by means of the four-wave mixing (FWM) spectroscopy. It is shown that the coherent couplings between the vibronic modes are feasible on demand. The experimental results are compared with theoretical calculations performed by introducing all possible Liouville space pathways.

2. Experimental

Spheroidene was isolated from the cells of *Rba. sphaeroides* 2.4.1 and then purified by recrystallising twice from *n*-hexane [22]. For the optical measurements, spheroidene was dissolved in tetrahydrofuran (THF). A home-build noncollinear optical parametric amplifier (NOPA) pumped by a femtosecond Ti:sapphire regenerative amplifier (Spectra Physics, Hurricane) was used as the excitation light source for the FWM measurements. The pump pulses in the triangular configuration were focused onto the surface of a sample flow-cell. The temporal delay of each pulse was controlled using a translation stage with a stepping resolution of 20 nm, which corresponds to a temporal step of 0.13 fs. In all FWM measurements reported here, the pulse widths measured using the cross-correlation technique were better than 16 fs. More details of the NOPA together with the optical setup have been described in Ref. [23]. All the optical measurements were performed at room temperature.

3. Results and discussion

Figures 1(a) and 1(b) compare the FWM signals at different coherent periods τ (the temporal separation between the first and second pulses). The Figure 1(a) shows the transient grating (TG) signal ($\tau = 0$) from spheroidene in THF. The abscissa shows the temporal separation between the second and third pulses (the population period T). Following the so-called coherent spike at $T = 0$, coherent oscillations with a period of a few tens of femtoseconds are clearly observed. The origin of the oscillation can be readily understood from the fast Fourier transform (FFT) spectrum of the signal, as shown in Fig. 2(a). The coherent spike and the slowly varying background were subtracted from the signal prior to the FFT analysis. By comparing the FFT spectrum with the conventional Raman spectrum shown in Fig. 2(a) and 2(c), respectively, we can conclude that the dominant peaks labelled as ν_1 and ν_2 are due to symmetric stretching modes of the C = C and C − C bonds, respectively [24, 25]. A further Raman band ν_3 reflects the methyl-in-plane rocking mode.

The FWM signal shown in Fig. 1(b) was taken by setting $\tau = -50$ fs. In the typical three-pulse photon-echo experiments, the signal is detected along the phase-matching direction $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$, where pulse 1 possessing the momentum vector $\boldsymbol{k}_1$ excites the sample first, followed by pulse 2 with $\boldsymbol{k}_2$. However, since pulse 2 arrives at the sample prior to pulse 1 in the present experiment, the coherent period is

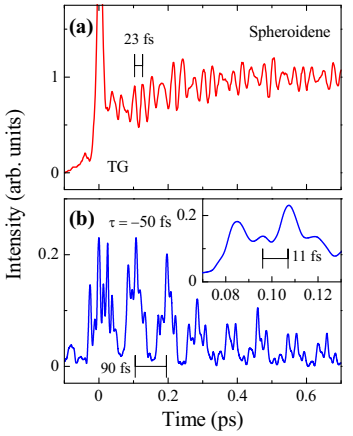

Fig. 1 (a) Temporal profile of the FWM signal in the TG configuration ($\tau = 0$). (b) The FWM signal at $\tau = -50$ fs. The magnified signal is also shown in the inset. The period of the fast oscillations is about a half of that in Fig. 1(a) (~11 fs) with the envelop of about 90 fs.

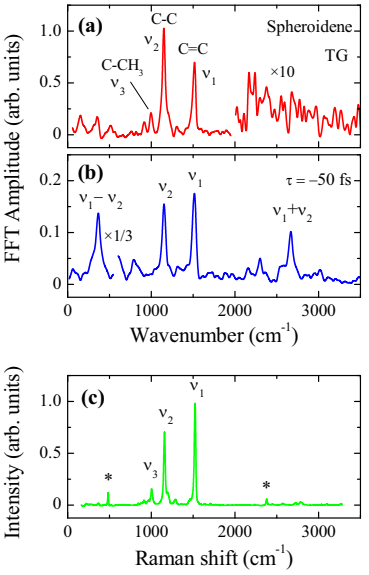

Fig. 2 (a) and (b): FFT spectra of the FWM signals shown in Figs. 1(a) and (b), respectively. In addition to the fundamental modes, the coupled modes are clearly observed in Fig. 2(b). (c): The resonance Raman spectrum for comparison. The peaks marked by asterisks are instrumental ghost lines.

represented with a negative sign. Namely, this pulse sequence is the same as the so-called virtual photon-echo experiment [26]. In Fig. 1(b), the total intensity of the signal is about 5 times weaker than that shown in Fig. 1(a) and the slowly varying background has almost vanished. However, the coherent oscillations are still clearly observed. The FFT spectrum of the signal in Fig. 1(b) is shown in Fig. 2(b). In addition to ν_1 and ν_2, two distinct peaks at 366 and 2668 cm^{-1} are observed. Since the energies of these peaks agree quite well with the difference and sum of ν_1 and ν_2, they reflect the coherent coupling between the vibronic oscillations, i.e., $\nu_1 - \nu_2$ and $\nu_1 + \nu_2$. Note that the energies 366 and 2668 cm^{-1} respectively are equivalent to 91 and 12 fs in the time domain. The envelope of the signal in Fig. 1(b) reflects the $\nu_1 - \nu_2$ modes, while the fast oscillations shown in the inset in Fig. 1(b) reflect the $\nu_1 + \nu_2$ modes. It should be emphasized that the coupled modes are inactive in the conventional Raman measurement, but can be excited simply by controlling the temporal separation of the ultrashort pulses: even a figure print of the $\nu_1 + \nu_2$ mode cannot be observed in Fig. 2(a). The experiments have been repeated at various τ. We found that the relative intensities of the coupled modes to the fundamental modes have the maximum values around $\tau = -50$ fs.

The experimental results have been compared with numerical calculations [27]. The FFT spectra of the calculated FWM signals are shown in Fig. 3. The parameters used for the calculation is the same as those used in Ref. [7]. The spectrum in the TG configuration reproduces the experimental result shown in Fig. 2(a), i.e., the fundamental modes ν_1, ν_2 and ν_3 appear clearly. With an increase of the coherent period, new peaks due to the coherent coupling between the vibronic oscillations are observed, which is qualitatively consistent with the experimental results. However the calculated results contain quantitative differences compared to the experimental data. For example, the coupled modes are dominant around $\tau = -50$ fs in the experiment, while those in the calculations are maximal around -10 to -20 fs. We have repeated the calculations changing the parameters, but could not reproduce the experimental results quantitatively. This fact indicates an additional effect should be introduced to the model to fully explain the experimental data set.

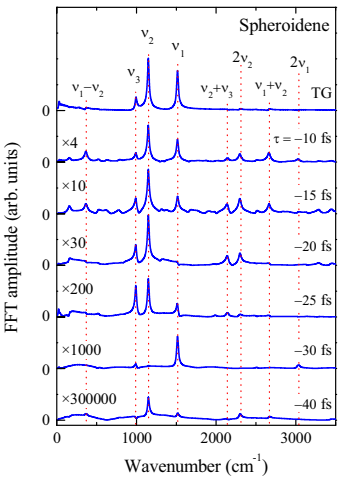

Fig. 3 Numerically calculated FFT spectra. The numbers on the right indicate the coherent periods τ. In addition to the fundamental modes, the coupled modes appear around -10 to -20 fs.

Since the experimentally observed signal is the sum of the response functions that reflect all the possible optical pathways, the calculation may have droped some of the optical responses. Bearing this idea in mind, a plausible origin of these differences may be due to higher-order interactions, namely the fifth-order polarizability plays a role. Although the FWM signal is obtained along the $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$ direction, this also satisfies the phase matching condition for the fifth-order interaction, e.g., $-\boldsymbol{k}_1 + (\boldsymbol{k}_1 - \boldsymbol{k}_1) + \boldsymbol{k}_2 + \boldsymbol{k}_3$, $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + (\boldsymbol{k}_2 - \boldsymbol{k}_2) + \boldsymbol{k}_3$, and $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3 + (\boldsymbol{k}_3 - \boldsymbol{k}_3)$. In this case, some more sets of response functions must be included and this results in a change of the calculated result. Such a signal has been experimentally reported by in Refs. [28-30], while the coupled modes have not been discussed. Further, as we have already reported, since the fifth-order signals from

carotenoids (six-wave mixing signals) can be easily observed by the naked eyes [23], the higher order term can have significant amplitude. Since these extended calculations require substantial work on methodology development, we leave them for future study.

In summary, we have observed the coherent vibronic oscillations of spheroidene in the ground state. It was demonstrated that the strong coupling between the vibronic modes can be attained simply by tuning the pulse separations. To the best of our knowledge, this is the first report on the excitation of the coupled mode on demand between the coherent vibrations.

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